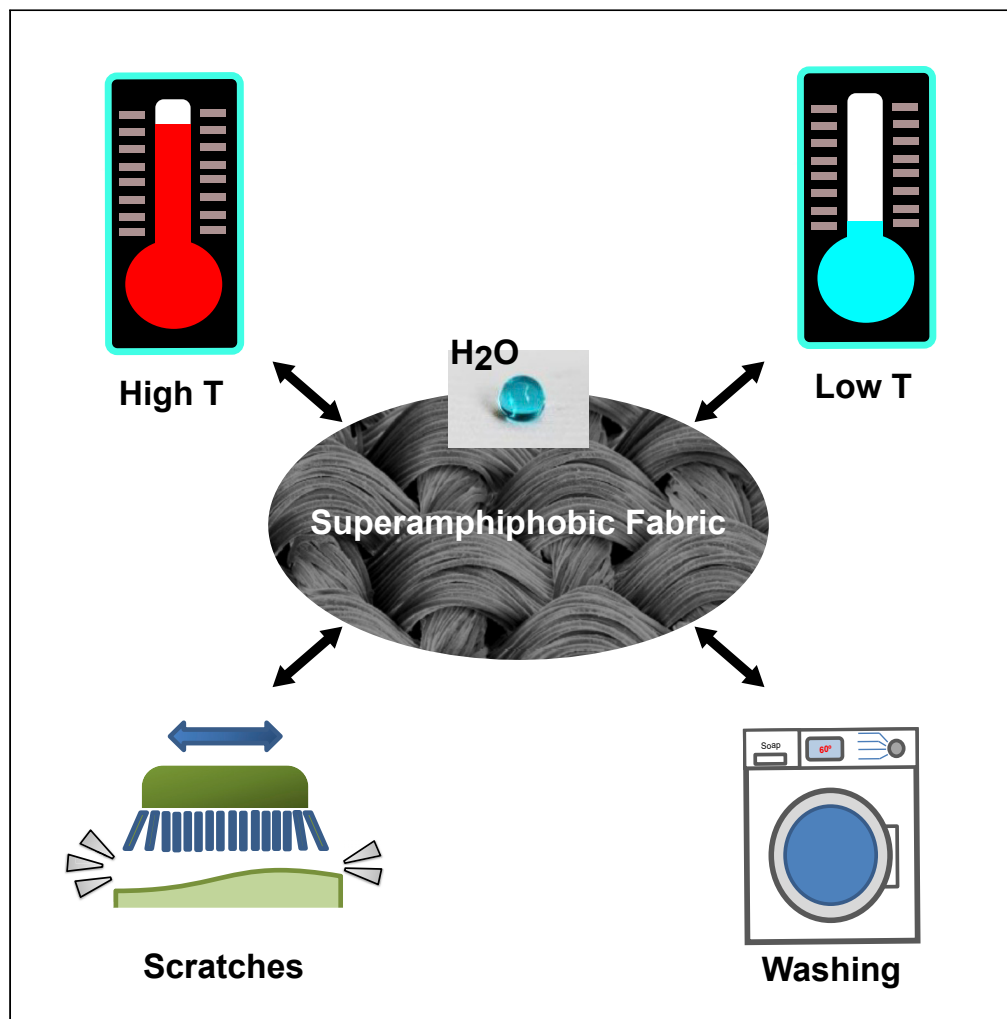


Article

Super liquid repellent coatings against the everyday life wear: Heating, freezing, scratching



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Highlights

Durability of a
superamphiphobic fabric
against common sources
of wear is tested

The fabric preserves water
repellence after freezing,
ironing, scratching, and
washing

The performance comes
from the synergy between
fabric and nanofilaments'
properties

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Article

Super liquid repellent coatings against the everyday life wear: Heating, freezing, scratching

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SUMMARY

Super liquid repellent coatings are among the most promising candidates for self-cleaning surfaces for indoor and outdoor applications. However, the characteristic nano- and micro-scale protrusions can easily be damaged. Improving the durability of these coatings belongs to the most important challenges to increase the coating's application potential. Here, we show that commercial polyester fabrics coated with silicone nanofilaments maintain their self-cleaning properties throughout repeated freezing-unfreezing cycles, ironing, and mechanical stress. The coating improves the heat resistance of the fabric. The surface keeps its water repellency until the fabric is almost destroyed by scratching with sandpaper or a metal sponge. The excellent performance results from the synergetic effects of i) the interwoven structure of the fabric and ii) the intrinsic hydrophobic and flexible nature of the fabric and of the nanofilaments coating. The combination of these factors generates a product which overcomes the most claimed drawbacks of super liquid repellent coatings.

INTRODUCTION

Super liquid repellent coatings (Feng and Jiang, 2006) have been proposed as suitable solutions for applications where self-cleaning (Furstner et al., 2005; Ganesh et al., 2011), anti-biofouling (Geyer et al., 2019) or anti-icing properties (Farhadi et al., 2011; Kim et al., 2012; Latthe et al., 2019a) are desired. Superhydrophobic (Onda et al., 1996; Feng et al., 2002; Lafuma and Quere, 2003) and superamphiphobic (Tuteja et al., 2007; Deng et al., 2012) coatings belong to the most well-known super liquid repellent coatings. Characteristic is that deposited drops roll off if the surface is tilted by a few degrees. Superhydrophobicity requires an appropriate combination of surface roughness in the (sub)micro-scale and low surface energy. Water repellency can be increased by adding nano-scale roughness (Nosonovsky and Bhushan, 2007) onto micro protrusions, mimicking the well-known morphology of the lotus leave (Neinhuis and Barthlott, 1997). To obtain superamphiphobicity, i.e. water and oil repellency (Feng and Jiang, 2006; Chu and Seeger, 2014; Yong et al., 2017), re-entrant surface curvature must be introduced (Tuteja et al., 2007).

Great effort has been put in improving the wetting performances of superhydrophobic (Erbil et al., 2003; Lau et al., 2003; Zhai et al., 2004; D'acunzi et al., 2010; Deng et al., 2011) and superamphiphobic (Srinivasan et al., 2011; Zhang and Seeger, 2011; Deng et al., 2012) coatings. At present, many of the proposed procedures are simple and cost-effective and repellency against low surface tension liquids as hexadecane (Geyer et al., 2017) has been reported. However, the durability (Verho et al., 2011; Zhu et al., 2011; Wang et al., 2020) and in particular the scratch resistance of super repellent coatings and its characterization (Paven et al., 2016) belongs to the major challenges (Cohen et al., 2016; Malavasi et al., 2015). Because of the small scale of their morphology, superhydrophobic and superamphiphobic coatings suffer from intrinsic mechanical stability. The fragile micro- and nano-protrusions can be damaged upon abrasion or application of mechanical stress in general. This is particularly severe if the underlying material is a high surface energy material (for example silica) and its surface energy is lowered by depositing a layer of fluoro- or alkyl-silanes. Often, even the scratch of a finger can cause mechanical or chemical damage with consequent loss of the initial wetting properties.

Many of the proposed applications (Zhang et al., 2008; Darmanin and Guittard, 2014; Latthe et al., 2019b) for superhydrophobic coatings require durability at outdoor environmental conditions. In countries with

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temperate climate, characterized by the alternation of the four seasons, this implies the necessity to withstand temperatures ranging from about -20°C to 50°C and several weather phenomena, like wind, rain, snow, frost, etc. Often, thermal excursion in winter ranges from temperatures below zero during night to several degrees above zero during daytime; under these conditions, coatings undergo many freezing-unfreezing cycles in few months' time. During freezing-unfreezing cycles, the protrusions suffer from stress due to the volume expansion of water under cooling. Apart from withstanding low temperature, many fabrics also need to withstand high temperatures and shear stresses as oftentimes they will be ironed. Therefore, the study of the resistance of superhydrophobic and superamphiphobic coatings under harsh indoor and outdoor conditions is crucial for their applications.

In the last years, super liquid repellent coatings have reached a remarkable degree of maturity (Zhou et al., 2013; Wang et al., 2020). Here, we show that fabrics coated with silicone nanofilaments (Zhang and Seeger, 2011) keep their excellent liquid repellency even after exposure to harsh operating conditions. In contrast to common expectations (Tian et al., 2016), the coating keeps its super liquid repellency despite the fact the nano- and micrometer sized protrusions were heavily damaged and the fabric locally fully destroyed.

Silicones (Zheng and McCarthy, 2010; Fink, 2013) belong to one of the most important classes of polymeric materials. Because of their mechanical, thermal, and chemical resistance, they are used to produce a broad range of materials, like resins, oils, elastomers, etc. Silicone nanofilaments have shown resistance to harsh chemical (Zimmermann et al., 2007; Geyer et al., 2017) environments and to UV irradiation (Zimmermann et al., 2007). Commercial polyester fabrics coated with silicone nanofilaments were still functional after exposure to urban environment for several months (Geyer et al., 2020) and maintained their good wetting characteristics until airspeed of 120m/s (Laroche et al., 2020).

Here, we demonstrate the endurance of the above-mentioned coating under repeated freezing-unfreezing cycles, after ironing, washing, centrifugation, and after severely damaging the coated fabric by continual scratches with sandpaper and a metal sponge. Notably, the coating improved the heat resistance of the fabric. The coated fabric also kept its good water repellency after mechanical abrasion until the fabric was almost fully destroyed. However, the fabric's superamphiphobic properties decrease after washing. Finally, we discuss why the three-dimensional coating of the fibers with silicone nanofilaments causes the remarkable performances of the fabrics.

RESULTS

Preparation of the superamphiphobic fabrics

Superhydrophobic and superamphiphobic fabrics were prepared by coating polyester fibers with silicone nanofilaments as reported by Geyer et al. (Geyer et al., 2017). The commercial fabric is approximately 160 μm thick and is composed of fibers with a diameter ranging from 8 to 15 μm (Figure 1A). The fabric becomes superhydrophobic after immersion in a solution of trichloromethylsilane in toluene with low water content, in the order of 150 ppm. Silicone nanofilaments (Artus and Seeger, 2014) grow on the surface of the polyester substrate by means of hydrolysis of the Si-Cl bonds followed by condensation of the Si-OH bonds (Figures 1B and 1C, for further details see the methods section). This corresponds to the reaction for the synthesis of polysiloxanes. The presence of methyl groups located at the interface with air causes the low surface energy of the nanofilaments required for superhydrophobicity. Figure 1B shows the typical morphology of silicone nanofilaments synthesized on polyester fabric. Note that nanofilaments evenly coat the surface of the fibers, including the sides and underside of the fibers. Coated fabrics show a receding contact angle for water higher than 150° and roll-off angle well below 10° (Geyer et al., 2017).

Superamphiphobicity is achieved after coating the nanofilaments with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (for details see methods section). After fluorination, the coated fabrics also repel low surface tension liquids like diiodomethane and hexadecane (surface tension of 50,8 and 27,5 $\text{mN}\cdot\text{m}^{-1}$, respectively) (Geyer et al., 2017). The insets in Figure 1B show, from left to right, that 10 μL drops of water, diiodomethane, and hexadecane on a superamphiphobic fabric keep their spherical shape.

Endurance at low temperatures: Cyclic freezing and unfreezing experiments

The anti-icing performances of superhydrophobic surfaces have been questioned repeatedly (Kulinich et al., 2011; Farhadi et al., 2011; Kreder et al., 2016; Jung et al., 2011; Cao et al., 2009). For example, Kulinich

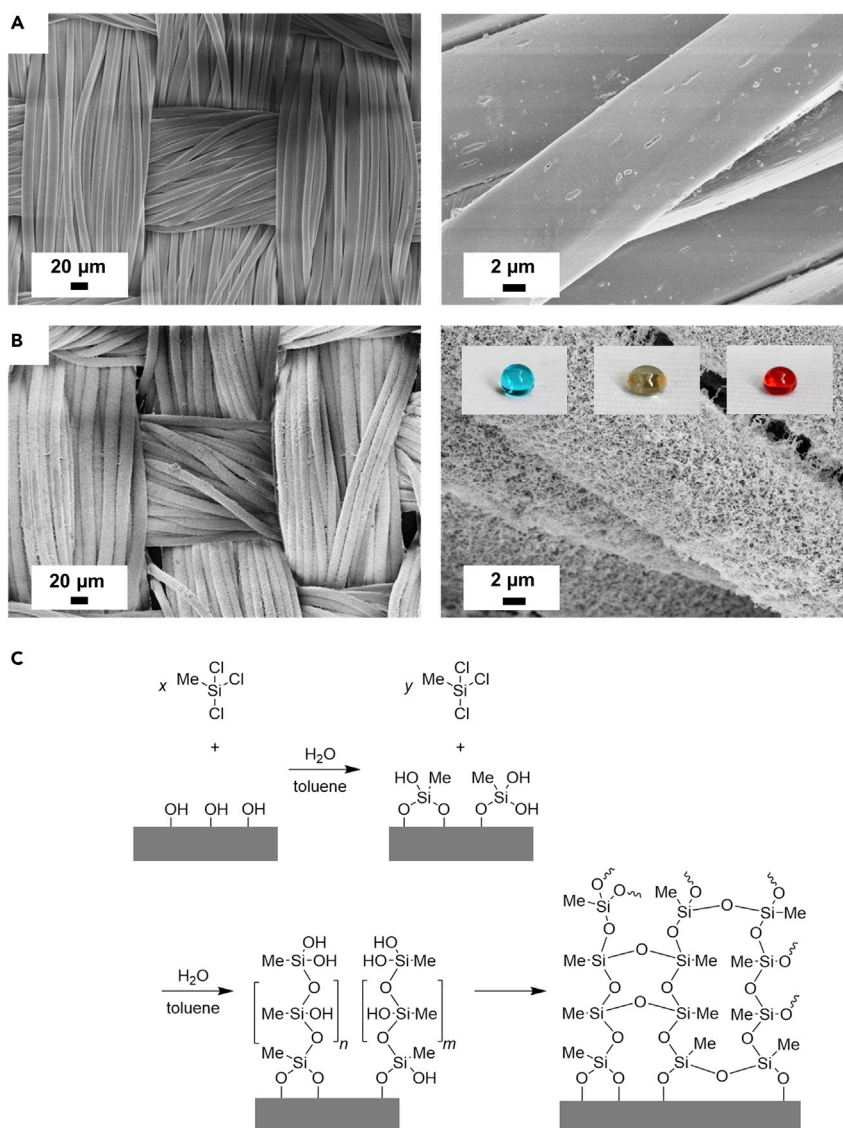


Figure 1. Preparation and characterization of the superamphiphobic fabrics

(A and B) (A) Low and high magnification Scanning Electron Microscope (SEM) images of the fabric before coating and (B) after coating with silicone nanofilaments. Insets in B (right figure): from left to right, 10 μ L drops of water (dyed with methylene blue), diiodomethane and hexadecane (dyed with oil red) on a superamphiphobic fabric.

(C) Reaction scheme of the synthesis of silicone nanofilaments, adapted from the Figure S3 of Geyer et al. Adv. Mat. 29, 6 (2017) (Geyer et al., 2017).

et al. (Kulinich et al., 2011) found that their surfaces were damaged by repeated freezing-unfreezing cycles because of the continuous stress the asperities undergo during freezing and thawing.

To gain insight into the freezing resistance of coated fabrics, we used two liquids, water, and cyclohexane. Water was chosen because it is omnipresent in outdoor situations and because of its thermal anomaly (Hawkins, 1976); the density passes a maximum at 4°C. For comparison, immersion was also carried out in cyclohexane, a liquid whose volume decreases with decreasing temperature without anomalies. Furthermore, we aimed to understand whether the presence of an air cushion alters the wetting properties of the coated fabric. Immersion of a superamphiphobic fabric in water or cyclohexane always resulted in the formation of a visible shiny layer, named *plastron*, Figures 2A and S1. This wetting configuration is also termed Cassie state (Cassie and Baxter, 1944). To freeze the fabric in absence of an air cushion, it needs to be pre-

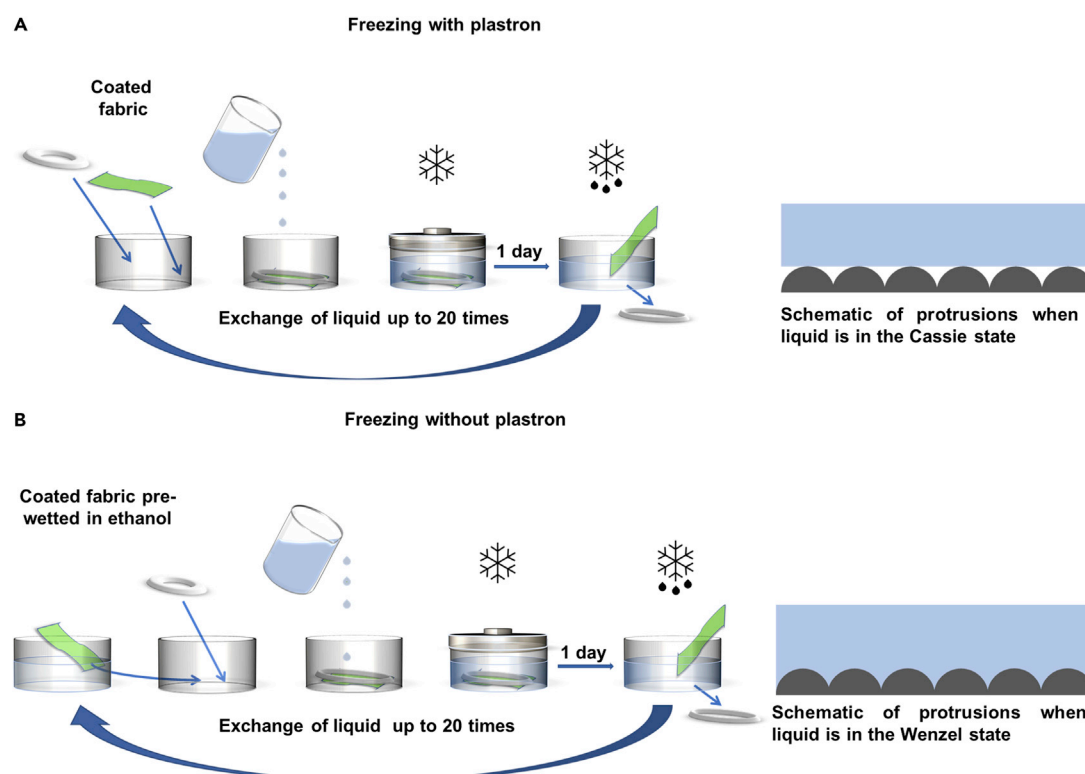


Figure 2. Sketch of the freezing-unfreezing cycles

Illustration of the freezing-unfreezing experiments with (A) plastron and (B) without plastron. A sample of coated fabric is immersed in the liquid (water or cyclohexane) and put in a freezer for 24 hr at a temperature of -21°C . After thawing, the liquid is exchanged. This procedure is repeated in the two different wetting configurations 20 times. In between, the fabric was characterized by roll-off angle and receding contact angle measurements. To freeze the coated fabric without plastron, the sample is pre-wetted in ethanol. Right images: schematic of the Cassie and Wenzel states. In the experiment with plastron (Cassie state), liquid partially rests on the air cushion and partially on the top faces of the coated fibers. In the Wenzel state the liquid wets the coated fibers. See also [Figures S1](#) and [S2](#).

wetted in ethanol. The low interfacial tension of ethanol (22 mN/m) resulted in complete wetting of the coated fabric, [Figure 2B](#). This wetting configuration is termed Wenzel state ([Wenzel, 1936](#)).

The dry and Wenzel wetted coated fabrics were placed in a weighing glass bottle. The fabrics were weighted with a Teflon ring to remain at the bottom of the bottle ([Figure S2](#)). If the coated fabric is in the Cassie state, buoyancy would cause the fabric to rise. After closing the weighing bottle, the samples were placed in a deep freezer at a temperature of -21°C ([Figure 2](#), left side) for 24 hr. After unfreezing, the liquid was removed; Cassie wetted samples were dry, whereas Wenzel wetted samples needed to be dried. This procedure was repeated 20 times for each fabric. Wettability was characterized before the first and after various numbers of freezing-thawing cycles by measuring the roll-off angles and receding angles for water and hexadecane ([Figure 3](#)). Advancing contact angles were not measured because on superhydrophobic/superamphiphobic surfaces liquid drops show an angle close to 180° , which cannot be measured with a contact angle goniometer ([Schellenberger et al., 2016](#)).

When water is used as the probe liquid, the wetting properties of the samples remain unchanged within experimental accuracy. Independent of the presence or absence of a plastron during freezing, the roll-off angle is $2.5^{\circ} \pm 1^{\circ}$, and the receding contact angle is $155^{\circ} \pm 4^{\circ}$. When the probe liquid was hexadecane ([Figure 3B](#)), the roll-off angle increased from approximately 10° to 18° or 26° and the receding contact angle decreased from 142° to 130° or 120° , respectively. The most affected fabric being the one immersed in cyclohexane with plastron. However, this fabric also showed slightly worst wetting properties before freezing.

To evaluate possible mechanical damage of the coating during freezing-unfreezing, the fabrics were investigated by scanning electron microscopy (SEM). After 20 cycles of freezing and unfreezing, the coatings

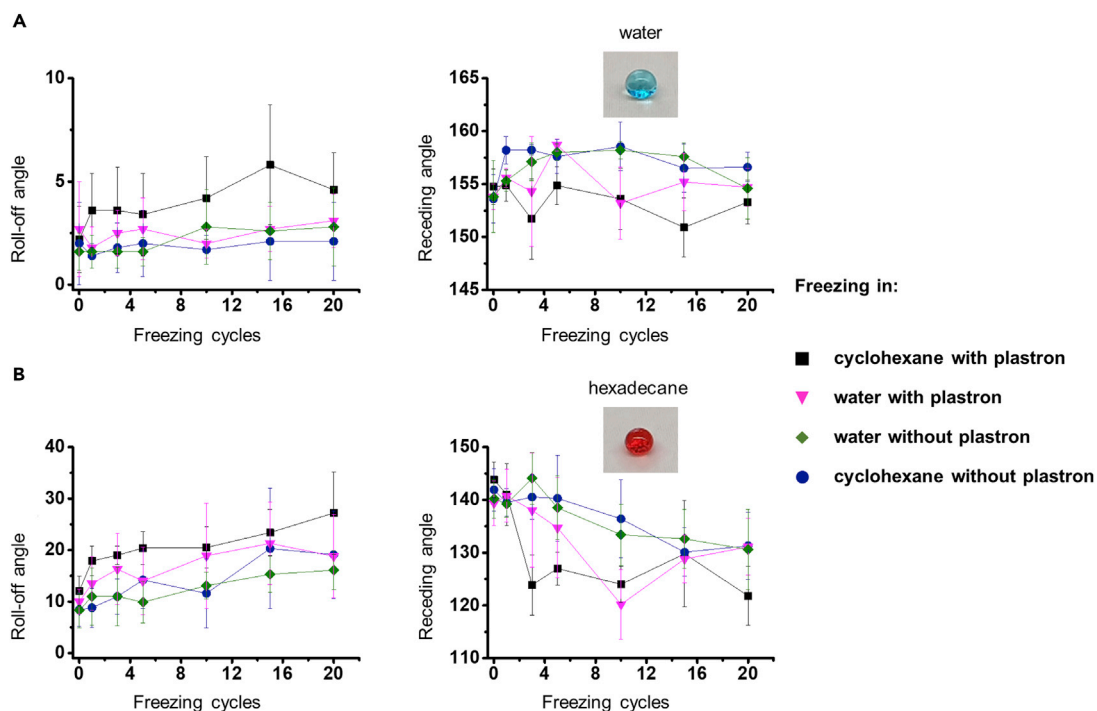


Figure 3. Wetting characterization of superamphiphobic fabrics before and after freezing-unfreezing cycles

Roll-off angle of a 5 μ L drop and receding angle as a function of the freezing cycles for the samples frozen in water and in cyclohexane with and without plastron, using (A) water and (B) hexadecane as probe liquids. The roll-off angle and receding contact angle is the average value of at least 12 and 5 measurements taken at different positions on the fabric respectively. The error bar is the standard deviation.

showed no deterioration (Figure S3), supporting the results obtained by contact angles measurements. Likely, the good freezing resistance results from the flexibility of the fibers and silicone nanofilaments. The stress can dissipate into the coating.

Endurance at high temperatures: ironing experiments

Superhydrophobic (table)cloths may need to withstand high temperature treatments and in particular ironing. To test the heat resistance of the coated fabrics, we ironed them using a commercial iron with 3 different heating levels. Level I corresponds to a maximum temperature of approximately 130°C and is recommended for delicate fabrics like silk, polyamide, and polyester. Level II reaches temperatures of about 175°C and is suitable for wool. Level III can reach up to 240°C and can be applied only to cotton and linen. After having ironed the fabrics for one minute at each heat level all fabrics remained superhydrophobic, Figure 4A. Even after ironing the fabric at a temperature as high as 240°C the shape and morphology of the coated fabric remained unchanged, Figure 4B. Contrary, the bare polyester fabric was irreversibly damaged, Figure 4C (Video S1). After having been ironed for one minute at 240°C (level III) the fabric shrunk and crumpled. Shrinking resulted in a tighter arrangement of the fibers (Figure 4C, right). Thus, the silicone filaments protect the polyester fabric from being heated up to 240°C. Likely, this is caused by the poor thermal conductivity of silicone and air.

Resistance to scratching, washing, and rubbing

Scratch resistance is the Achilles' heel of superhydrophobic and superamphiphobic coatings (Tian et al., 2016). Severe mechanical damage of the surface results in a loss of its super liquid repellency. To test for the scratch resistance of the coated fabrics, we abraded the fabrics using sandpaper and a metal sponge. The superamphiphobic fabric was scratched until macroscopic holes were visible by eye, Figure 5A. Notably, it can be observed that a water drop kept its spherical shape, Figures 5B and 5C. To correlate the wetting properties with the level of damage, we measured the roll-off and the receding contact angle after 25, 50, and 90 scratches. After 25 scratches, the SEM images already visualize broken fibers (Figures 5D–5F, and S4). After 90 scratches, the fabric was perforated (Video S2). The damaged fabric maintains

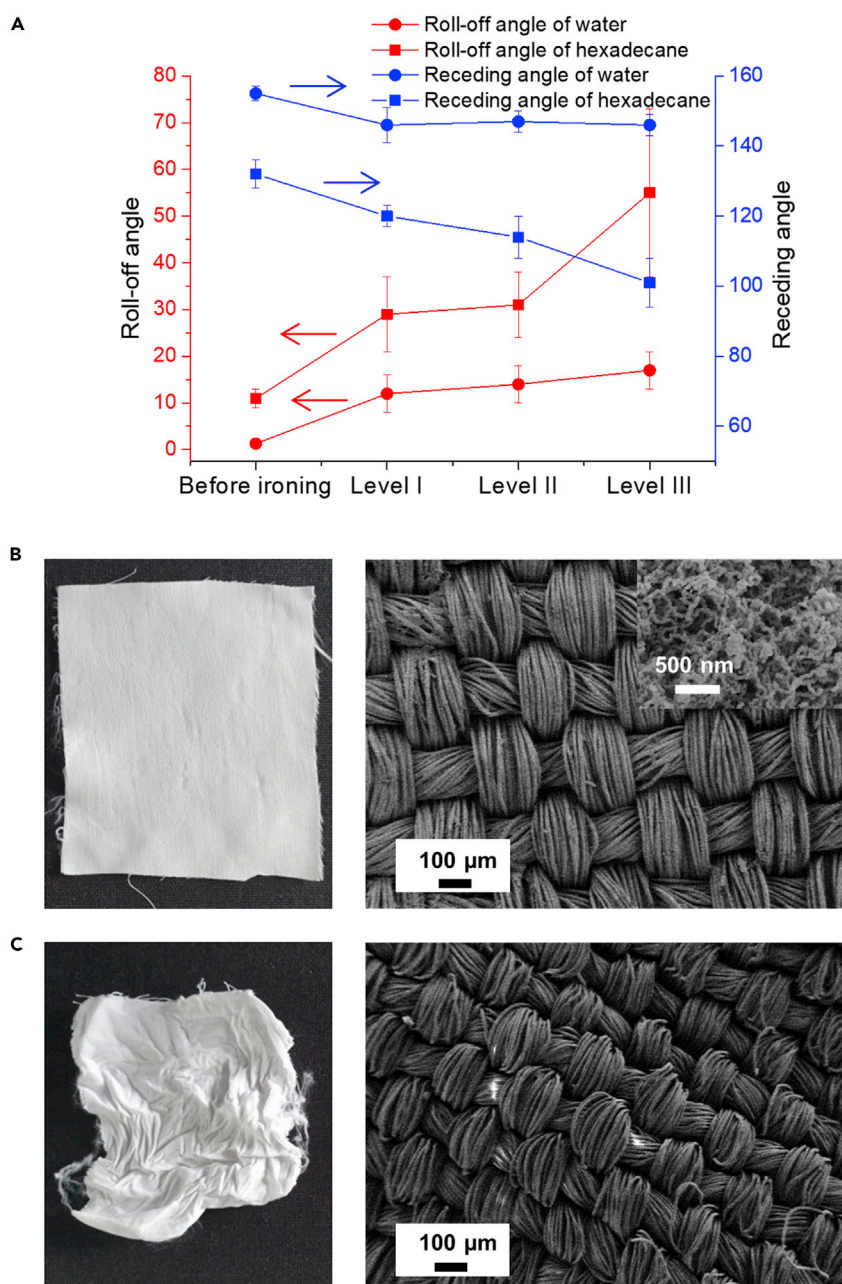


Figure 4. Characterization of the superamphiphobic fabrics after ironing experiments

(A) Roll-off angle and receding contact angle of the superamphiphobic fabric before and after having been ironed for one minute at heating level I ($T_{\max} = 130^{\circ}\text{C}$), level II ($T_{\max} = 175^{\circ}\text{C}$), and level III ($T_{\max} = 240^{\circ}\text{C}$). For the measurements of the roll-off angle, a drop volume of $5\ \mu\text{L}$ was used. The roll-off angle and receding contact angle is the average value of at least 10 and 5 measurements taken at different positions on the fabric respectively. The error bar is the standard deviation. (B) Optical image (left) and SEM image (right) of a coated fabric after it has been ironed at level III for one minute. Inset in (C): high resolution image of the nanofilaments after the fabric has been ironed at level III for 1 min. (C) Optical image (left) and SEM image (right) of a sample of bare polyester fabric after it has been ironed at level III for one minute. The dimensions of the fabrics in the optical images are $6 \times 7\ \text{cm}^2$.

its super repellency toward water even in proximity of the point of rupture (Figures 5B, 5C, and 5G). However, after abrasion the roll-off angle increased to 12° for a $10\ \mu\text{L}$ sized drop. Partially, the increase of the roll-off angle is due to damage induced topographical inhomogeneities. The drop preferentially rests in

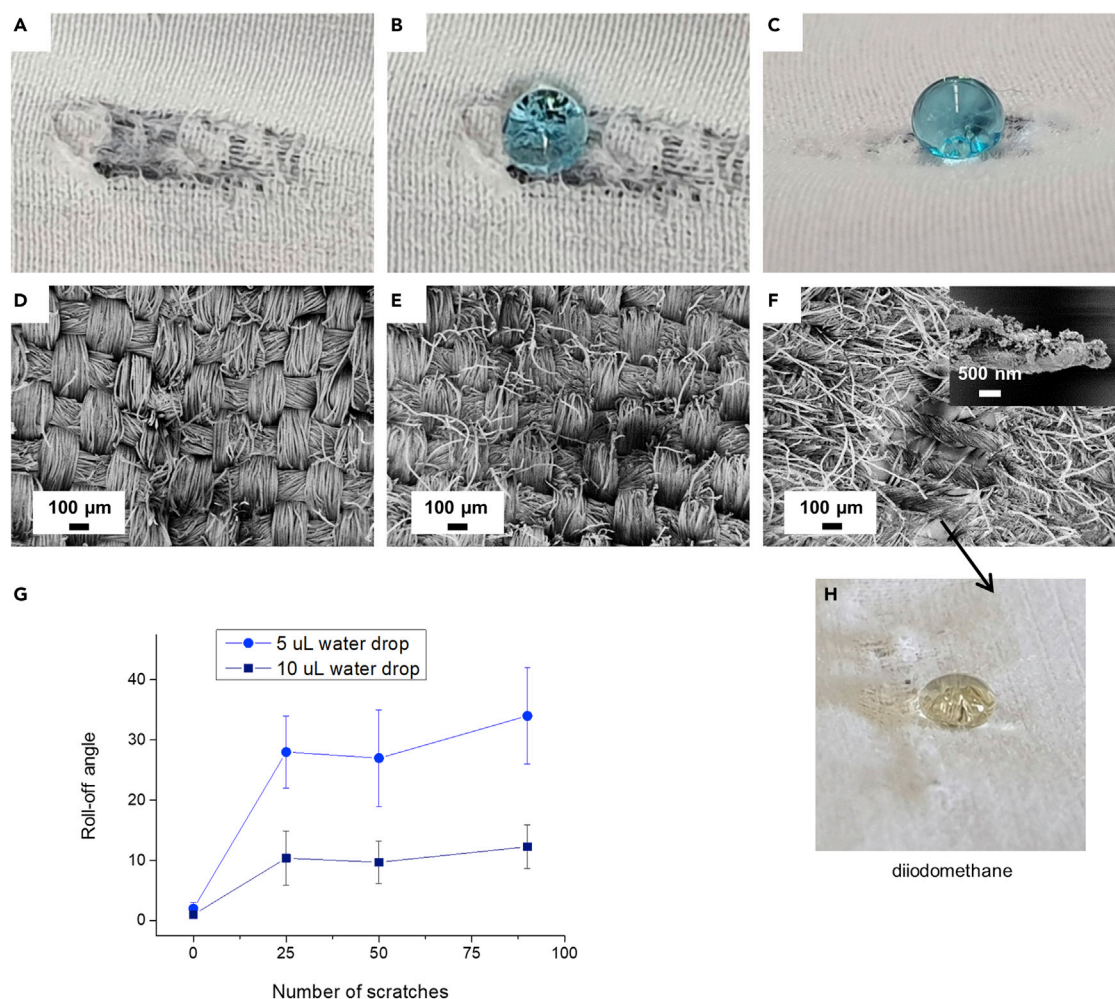


Figure 5. Characterization of the superamphiphobic fabric after scratching experiments

(A) Images of the fabric pierced after having been scratched with sandpaper.

(B–F) (B) Top view and (C) side view of a 15 µL water drop lying on the most damaged area. SEM images of the coated fabric after (D) 25, (E) 50, and (F) 90 scratches. Inset in (F): high magnification of the tip of a broken and scratched fiber.

(G) Roll-off angles of the coated fabric as a function of number of scratches and in dependence of the drop size. The roll-off angle is the average value of at least 10 measurements taken at different positions on the fabric. The error bar is the standard deviation.

(H) Photo of a 15 µL diiodomethane drop on the 90 times scratched fabric. The drop is deposited on the most damaged region.

grooves (Figure 5B). The influence of the topographical inhomogeneities on the wetting properties is therefore more pronounced for the 5 µL sized drops. A second reason for the increase of the roll-off angle is caused by local abrasion of the filaments. Some fibers are not fully coated by filaments any longer, Figures S4 and S5. On the damaged spots, the surface energy increases because the drop contacts methyl groups instead of fluorine. Because of the chemical compatibility of methyl groups and hexadecane, a deposited drop of hexadecane was rapidly adsorbed by the fibers. However, not all filaments were abraded. In particular, the side and underside of the fibers remained coated by filaments. This can even hold for the tip of ruptured fibers, inset Figure 5F. Therefore, even the most damaged sample kept its repellency toward diiodomethane (see Figure 5H and end part of Video S2 in the supplementary information). Notably, water repellency is preserved also in case of severe damage of a superhydrophobic fabric (non-fluorinated), as can be seen in Video S3. Video S4 shows a superamphiphobic fabric heavily abraded by means of a metal sponge, as commonly used in the kitchen.

A certain mechanical damage is experienced also by washing the superamphiphobic fabric in a commercial washing machine. Therefore, we tested the wetting properties of the fabrics after a typical washing cycle

(60°C, 1 hr 50 min, centrifugation 1200 rounds per minute) using a commercial detergent (see [methods](#) section and [Figure S6](#) for further details). During the washing procedure, the air plastron disappears, and the fabrics are fully wetted by the aqueous solution. After drying, the plastron recovers, and the fabrics exhibit self-cleaning properties toward water and diiodomethane ([Figure S6C](#)). The roll-off angle for water increased to approximately 27°. Hexadecane drops stick to the fabric.

The decrease of performance likely results from the combination of removal of filaments by shear stress and increase of the surface energy due to chemical contamination by surfactant. To simulate the influence of shear stress, we rubbed two superamphiphobic fabrics against each other. After 60 rubbing cycles, the fabric kept its superhydrophobicity but 6 μL sized hexadecane drops stick to the fabric ([Video S5](#), [Figure S7A](#)). Compared to the metal sponge and sandpaper tests, the two fabrics that were rubbed against each other have surface protrusions with identical spacings. This results in a larger effective contact area and thus more wear. Notably, centrifugation does not alter the morphology of the filaments. Images of the morphology of the filaments before and after centrifugation for 60 min at 10,000 rpm in water in a centrifuge (HERAEUS Multifuge X3R, tube diameter: 3cm) look identical, [Figure S7B](#).

DISCUSSION

We showed that commercial polyester fabric coated with silicone nanofilaments preserves its super repellency after exposure to many freezing-unfreezing cycles and to the highest temperature of a commercial iron. Notably, it even kept its superhydrophobicity after heavy damage with abrasive sandpaper and a metal sponge. Washing the fabrics in a washing machine altered the wetting properties most.

The reasons behind these noteworthy performances are manifold.

- The synthesis of silicone nanofilaments is performed in a liquid medium. The proposed reaction mechanism ([Artus et al., 2017](#)) only requires the presence of OH groups ([Artus and Seeger, 2014](#)). Therefore, silicone nanofilaments can homogeneously grow on fibers. Only areas where fibers make direct contact are excluded. If the silicone nanofilaments on the fibers' tops face are removed by scratching, they partially remain intact at the fibers' sides and at the underside. This is sufficient to prevent wetting of the fibers by solvents having an interfacial tension above approximately 50mN/m, e.g. diiodomethane.
- Another crucial factor is the hydrophobic nature of the polyester fabric and of the silicone nanofilaments. Even if nanofilaments are destroyed or rubbed off, the hydrophobicity of broken filaments and of the polyester fabric leaves a rough surface of low surface energy. The combination of both is sufficient to achieve superhydrophobicity.

The results demonstrate the relevance of coating a surface from all sides, i.e. to have a 3D coating. This is conceptually different from the intensively discussed dual scale roughness, where a micro- and nano-scale roughness is combined to improve mechanical stability and liquid repellency. As demonstrated the ability to evenly coat the sides and undersides of a surface is highly beneficial to design durable superhydrophobic surfaces.

- The flexibility of silicone is essential for the success of our freezing experiments. It allowed the silicone nanofilaments to resist the stress caused by the volume expansion of water. The high thermal resistance of silicone combined with the presence of the air cushion permits to obtain coated fabrics whose thermal resistance goes beyond the resistance of the bare material (polyester).

The combination of these aspects has a synergic effect on the overall wetting performances. In summary, this work demonstrates that the development of superhydrophobic and superamphiphobic surfaces has reached a considerable degree of maturity, permitting to propose them for many applications where durability is requested.

Limitations of the study

Despite the notable mechanical resistance, the nanofilament synthesis may be too slow for many industrial applications. The reaction takes 30 min to three hours.

Moreover, the superomniphobic fabrics are fluorinated materials. For several classes of materials, the coating with a fluorinated compound is prohibited.

Resource availability

Lead contact

Further requests for resources regarding this study will be fulfilled by the corresponding author, Doris Vollmer (vollmerd@mpip-mainz.mpg.de)

Material availability

Materials generated during this study may be requested from the authors.

Data and code availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the [supplementary information](#). Additional data related to this paper may be requested from the authors.

METHODS

All methods can be found in the accompanying [transparent methods supplemental file](#).

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.isci.2021.102460>.

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AUTHOR CONTRIBUTIONS

M.D'A. conceived and performed experiments and wrote the manuscript. A.S. performed the freezing-unfreezing experiments, their characterization and took the SEM images. K.I.H. supported in writing the manuscript. D.V. contributed to the experimental planning, data analysis, and manuscript preparation. All authors reviewed and approved the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental information

Super liquid repellent coatings

against the everyday life wear:

Heating, freezing, scratching

Maria D'Acunzi, Azadeh Sharifi-Aghili, Katharina Irene Hegner, and Doris Vollmer

TRANSPARENT METHODS

Materials

Trichloromethylsilane (TCMS, 99%), hexadecane (99 %) and ethanol (99,8%) were purchased from Sigma Aldrich. 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane (96%) and n-Hexane (95%) were obtained from Alfa Aesar and Fischer Chemicals, respectively. Cyclohexane (HPLC grade, 99,5) was obtained from VWR Chemicals. Toluene was purchased from both Sigma Aldrich and VWR Chemicals. The Karl-Fischer reagent used in this experiment was from Merck. Polyester fabric was purchased from Karstadt Warenhaus GmbH. Water used in all experiments was deionized (DI) and prepared by a Milli-Q system from Sartorius Arium pro VF. TCMS-coated polyester fabrics were activated in an oxygen plasma chamber (Diener Electronic Femto, 120 W, 2 min, 7 cm³/min oxygen flow rate). A coulometric Karl-Fischer Titrator (Mettler Toledo C20D compact KF coulometer) was used to determine the final water content of toluene. Weighing bottles with NS stopper (30 mm high, 80 mm diameter and 80 mm capacity) from Lenz Laborglas were used as glass chambers during icing- deicing experiments.

Preparation of superamphiphobic polyester fabrics

Polyester fabrics do not require any pre-treatment of their surface before coating with nanofilaments (Zimmermann et al., 2008, Zhang and Seeger, 2011). Surface hydroxyl groups are widely recognized as a prerequisite for achieving a homogeneous coating (Artus and Seeger, 2014). In case of polyester, hydroxyl groups are present in form of polymer chain end groups. Polyester fabrics were coated with nanofilaments by means of a two steps reaction. The first step makes the fabric superhydrophobic and second step makes it superamphiphobic.

Step 1: 1400 µL trichloromethylsilane (TCMS) was added to a Teflon reaction chamber containing 350 mL of toluene with water content of 150 ppm. Precise control of the water content of toluene was achieved by mixing i) toluene as received from the manufacturer (water content ranging from 30 to 80 ppm) with ii) water-saturated toluene. The water content was evaluated using a coulometer (Mettler Toledo C20 Compact KF coulometer). After having stirred the solution for 60 s with a magnet, a piece of fabric (11 cm length, 8 cm width) was immersed, and the reaction chamber was sealed. After 3 hours the coated fabric was rinsed with n-hexane and dried under nitrogen stream.

Step 2: The TCMS- coated fabric was activated in an oxygen reaction chamber for 2 min on each side (Diener Electronic Femto, 120 W, 2 min, 7 cm³/min oxygen flow rate). Afterwards 180 µL of 1H, 1H, 2H, 2H- perfluorodecyltrichlorosilane (PFDTs) was mixed with 350 ml of n-hexane in a Teflon chamber and the solution was mixed for 60 s. The activated TCMS- coated fabric was immersed in the solution and the chamber was sealed. After 20 min, the substrate was rinsed with n-hexane and dried under nitrogen stream.

Freezing-unfreezing experiments

Weighing bottles were cleaned with water and alcohol and dried by nitrogen gas. The coated fabrics were placed at the bottom of a weighing glass bottle (height = 30 mm, diameter = 80 mm, usable volume 80 ml). A Teflon ring was put on the fabric to keep them in place. The weighing bottle was filled with 62 ml liquid (water or cyclohexane). Afterwards the weighing bottles were closed by the glass cap and put in a refrigerator at -21°C. After 24 hours the bottles were removed from the refrigerator and kept at room temperature to melt the water or cyclohexane.

To perform the experiments in absence of plastron, fabrics were pre-wetted in ethanol before placing them in the weighing bottles. Putting the wet fabric into water or cyclohexane resulted in diffusion of ethanol into the liquid. The weighing bottle was left on air for half an hour to give ethanol the time to evaporate. Wenzel wetting was supported by the absence of a plastron. The freezing procedure was repeated 20 times on the same sample.

Ironing tests

Ironing tests were performed with the commercial iron Philips Azur excel plus 515. To verify the temperatures reached at every heating level, the iron was connected to a temperature sensor. At level I, iron heats up until the maximum temperature of 133°C. After that, it stops heating until the minimum temperature of 112°C. When the minimum is reached, it heats up again until 133°C. The same applies for level II ($T_{\max} = 175^{\circ}\text{C}$; $T_{\min} = 155$) and level III ($T_{\max} = 240^{\circ}\text{C}$; $T_{\min} = 214$). Superamphiphobic sample was ironed for one minute at each heating level and characterized every time with roll-off angle, receding angle and SEM.

Scratch tests

Scratch tests were performed with Klingspor sandpaper PS 33 P 120. A sample of superamphiphobic fabric (size 10 x 15 cm) was characterized with roll-off angle and receding angle measurement and subsequently divided in three pieces. The first piece was abraded 25 times with sandpaper, the second 50 times and the third one 90 times until rupture.

Washing machine tests

Washing machine tests were performed by a Bosch Avanti xx7 machine. Fabrics were washed together with 4 kg of common every-day laundry in such a way to fill the drum (see Figure S6). The detergent used was Denk Mit Ultra Sensitive from dm-drogerie markt in the amount of 50 g, as suggested on the package. The washing program was 'Synthetic clothes', corresponding to the following parameters: 1 hours and 49 minutes of total duration, temperature of 60 °C, final rinsing for 20 minutes and centrifugation at 1200 rounds per minute. After washing fabrics were dried in air and then roll-off angle was measured.

Rubbing tests

Two superamphiphobic fabrics were rubbed against each other 60 times. Repellency towards water and hexadecane was tested before and after the experiment.

Centrifugation tests

Superamphiphobic fabrics were introduced in centrifuge tubes with diameter of 3 cm and centrifuged at 10000 rotations per minute for 60 minutes (HERAEUS Multifuge X3R).

Advancing-receding contact angle measurements and roll-off angle measurements

Contact angle and roll-off angle measurements were conducted using a DataPhysics OCA35 goniometer. The roll-off angle was determined by depositing a 5 μL drop of probe liquid on the substrate placed on the goniometer stage and inclining the plane at a velocity of 1,7 $^\circ/\text{s}$. The angle at which the drop starts to move was detected. The reported values are the average of at least 10 measurements per sample. Receding contact angles were measured by gently depositing a 6 μL drop (water or hexadecane) on the sample. After that, 20 μL of the probe liquid was added and subsequently removed. During this procedure, drop shape was fitted using an elliptical fit and the contact angle versus drop volume was obtained.

Scanning Electron Microscopy (SEM) images

SEM images were taken using a Zeiss LEO 1530 Gemini SEM. To improve conductivity, samples were coated with 7 nm platinum layer using BalTec MED 020 modular high vacuum coating system.

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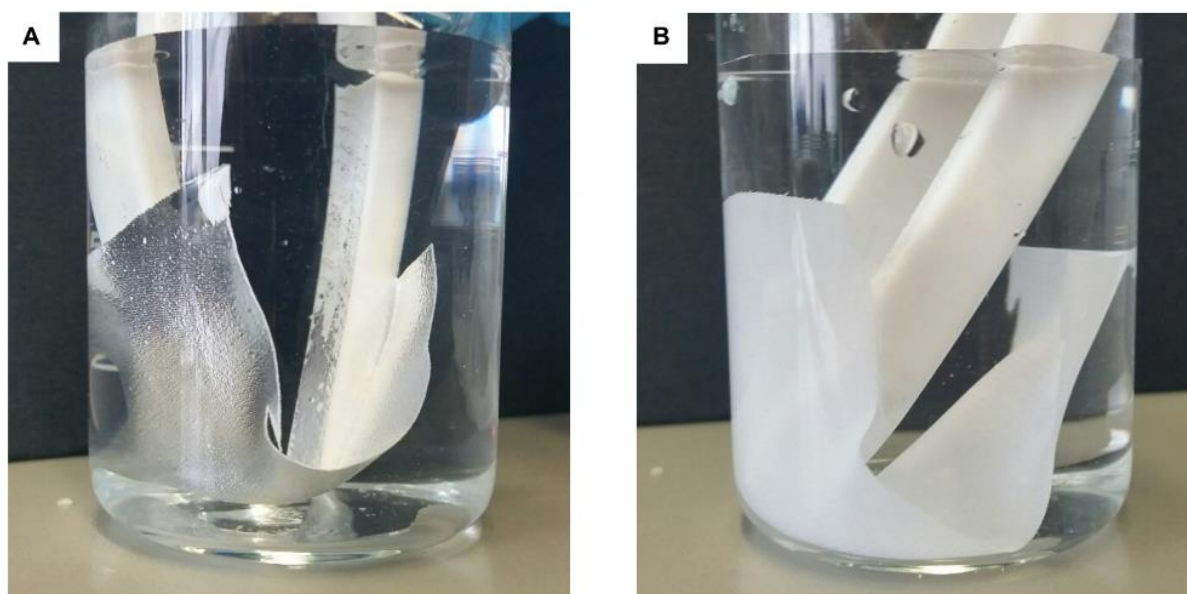


Figure S1. Coated fabric with and without plastron. Related to Figure 2.

Coated fabrics immersed in water with (A) plastron and (B) without plastron. The configuration with plastron is obtained by simple immersion of the superamphiphobic fabric in water. The configuration without plastron is obtained by previous wetting of the fabric in ethanol.

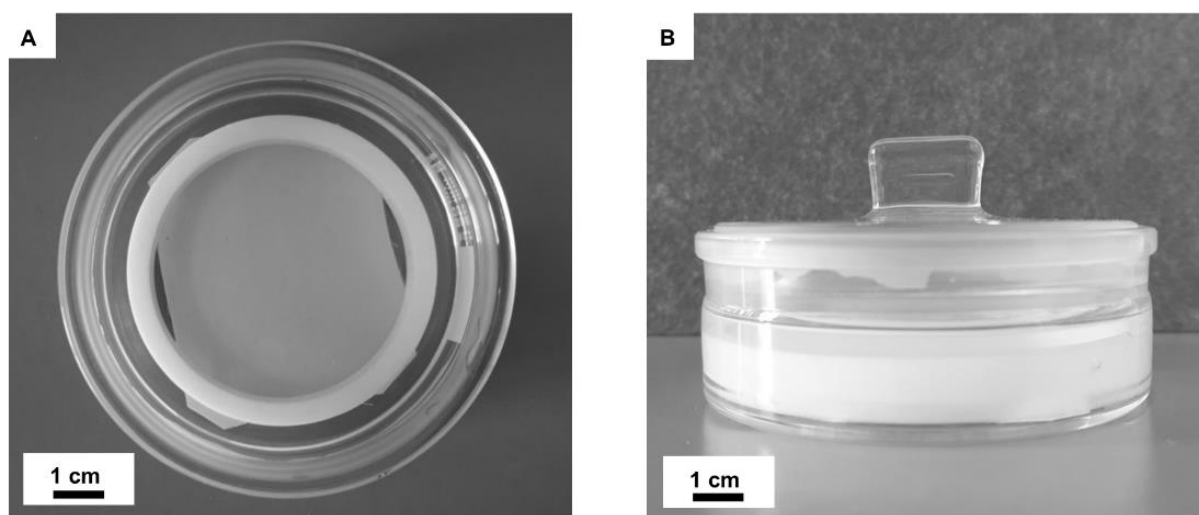


Figure S2. Setup of the freezing-unfreezing experiments. Related to Figure 2.

(A) Top view and (B) side view of the experimental setup built for the freezing-unfreezing experiments. The coated fabric is kept at the bottom of the weighing bottle by means of a Teflon ring.

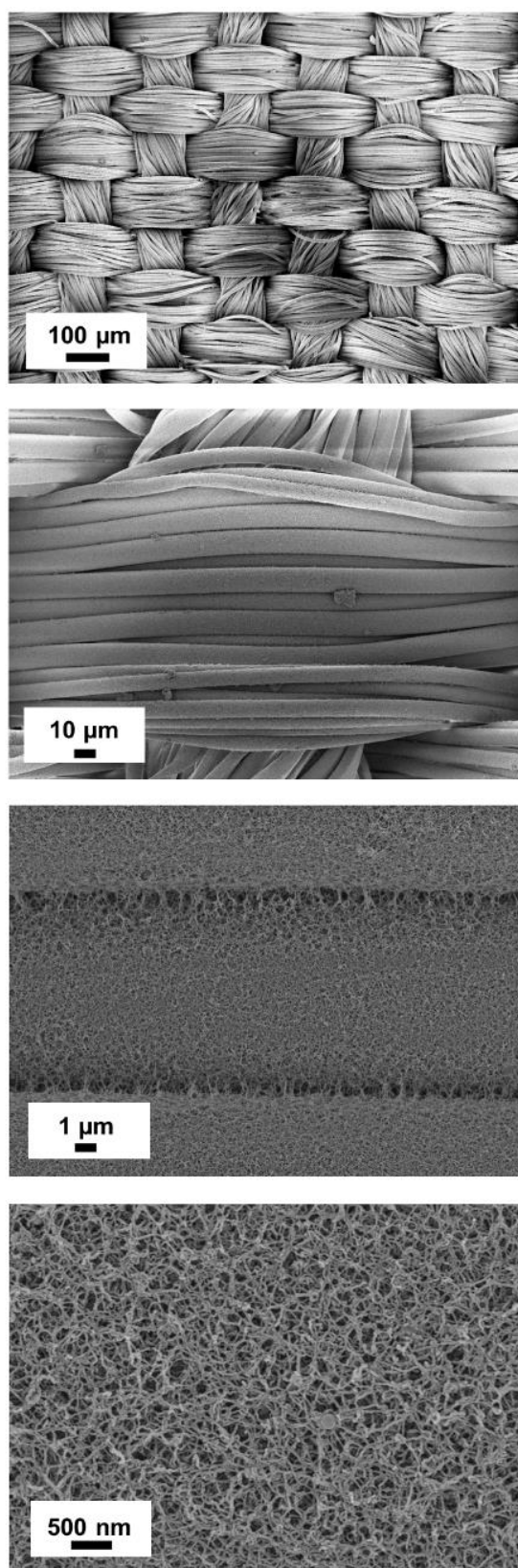


Figure S3. Coated fabric after freezing-unfreezing cycles. Related to Figure 3.

Representative SEM images at different magnifications of the superamphiphobic coated fabric after 20 freezing-unfreezing cycles. Sample shows no mechanical damage.

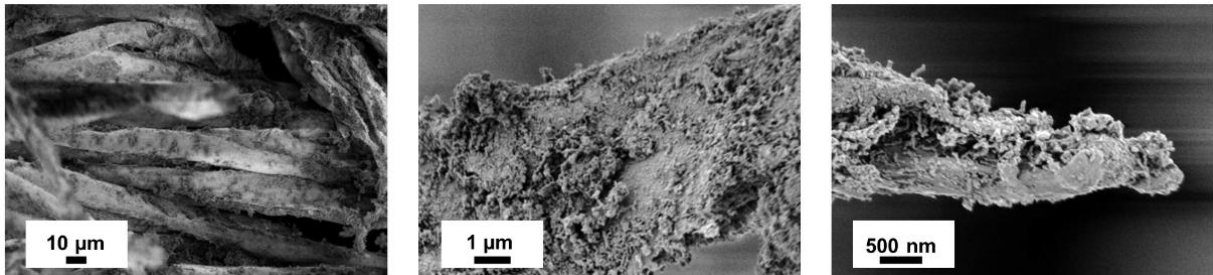


Figure S4. Coated fabric after scratching. Related to Figure 5.

SEM images at different magnifications of the broken fibers of a coated fabric after it has been scratched 90 times with sandpaper.

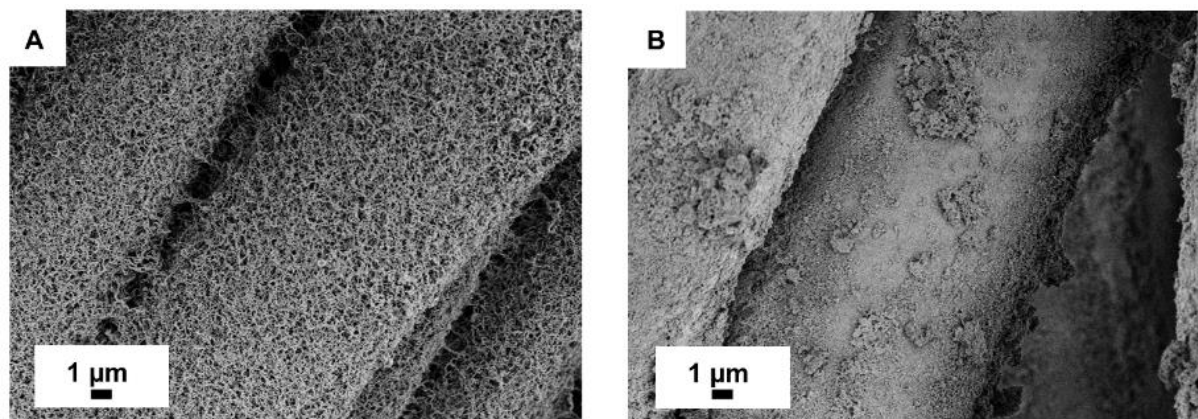


Figure S5. Coated fabric before and after scratching. Related to figure 5.

Comparison of SEM images of fibers (A) before and (B) after being scratched 90 times with sandpaper. The image in (B) shows regions where the coating was removed by the repeated scratches.

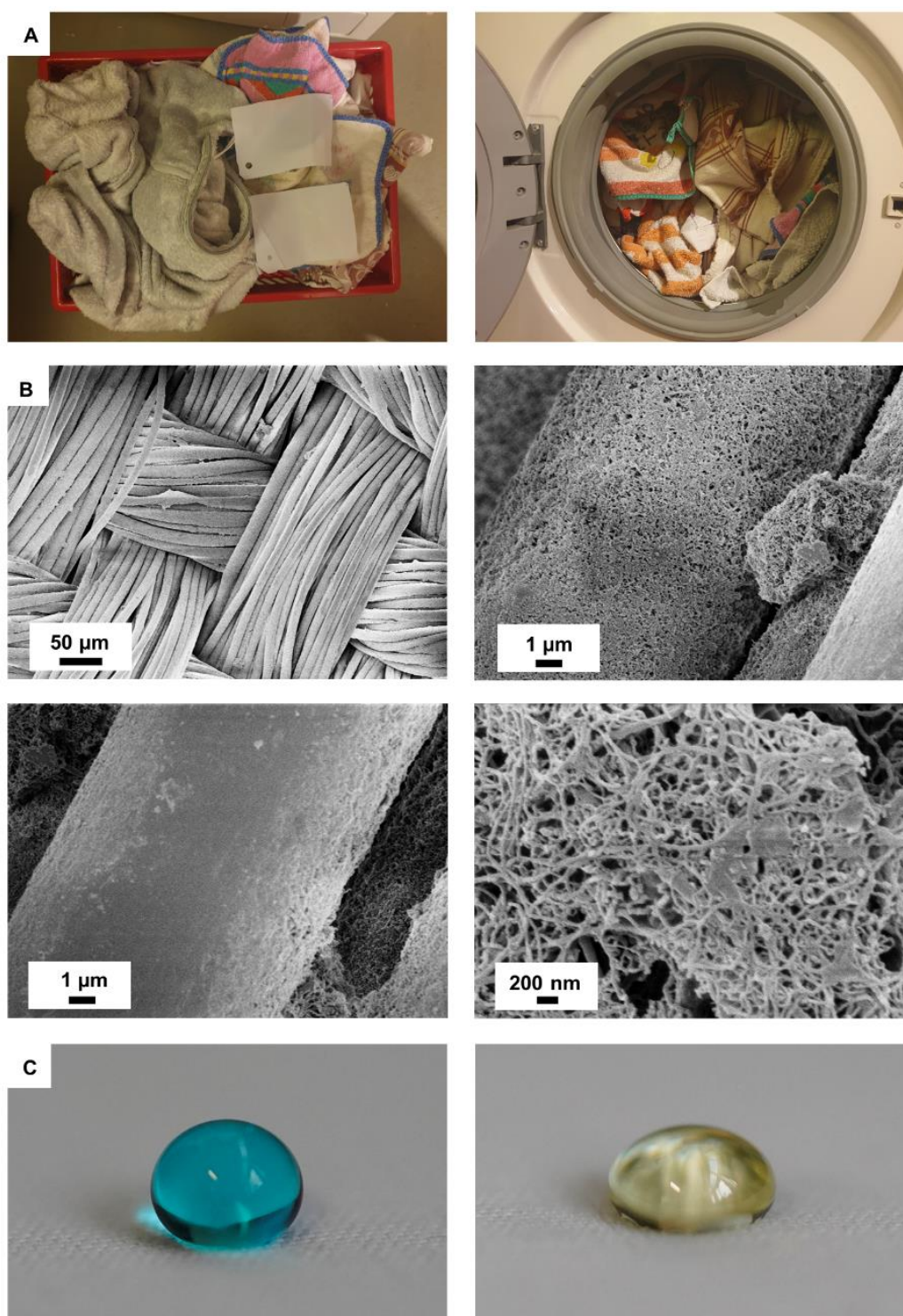


Figure S6. Washing tests. Related to Figure 5.

(A) Images of the load of laundry washed together with the superamphiphobic fabric. Dimensions of the fabrics: 9 x 13 cm² (B) Representative SEM images at different magnifications of the fabric after being washed. Mechanical damage is sporadically visible on the top side of the fibers. (C) Optical images of a 15 μL drop of water (left) and diiodomethane (right) deposited on the washed fabric. Water is dyed with methylene blue.

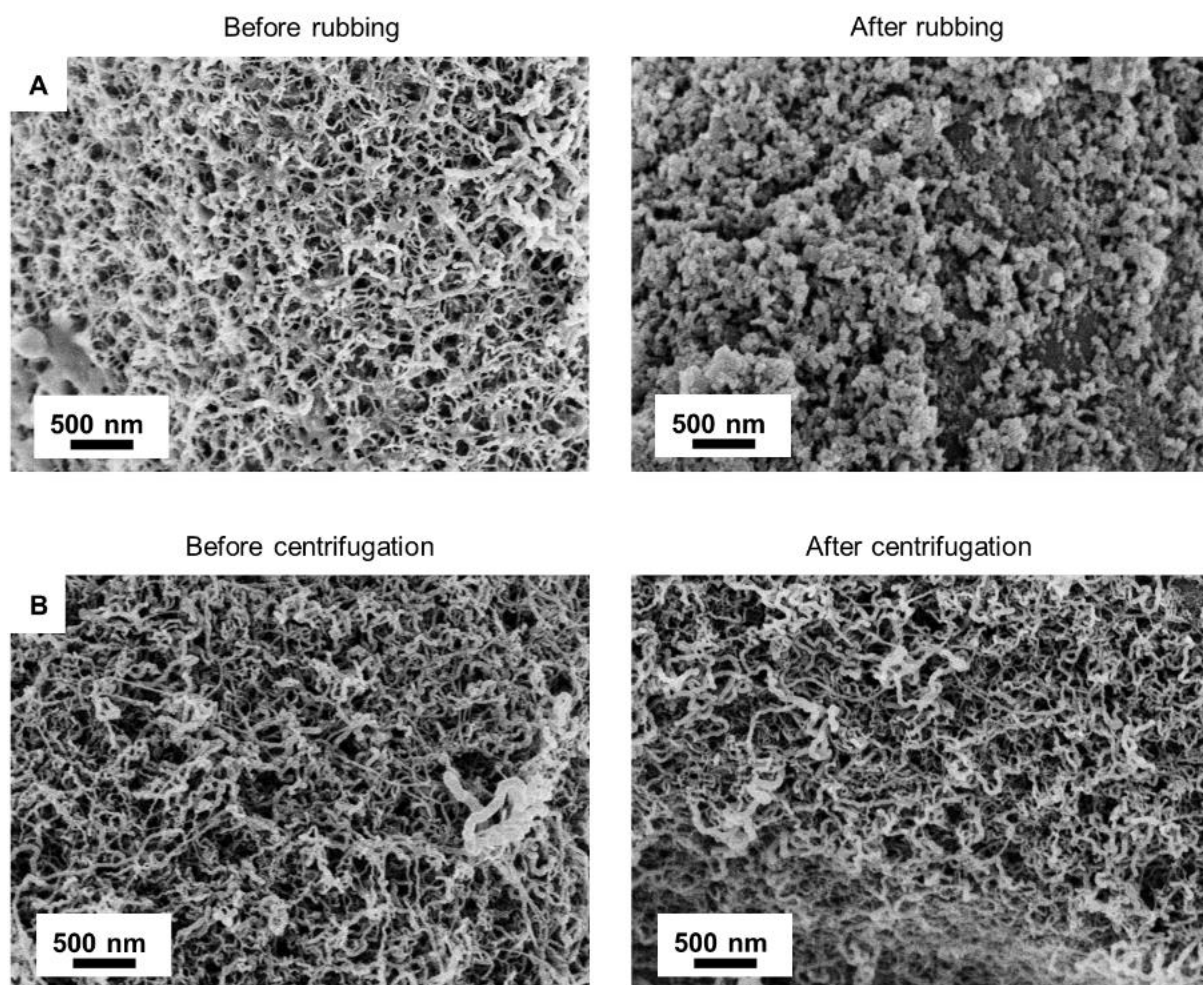


Figure S7. Rubbing and centrifugation tests. Related to Figure 5.

(A) SEM images of the superamphiphobic fabric before and after rubbing it 60 times against a second superamphiphobic fabric. (B) SEM images of superamphiphobic fabric before and after centrifugation in a centrifuge tube at 10000 rpm for 60 minutes.

PHYSICAL SCIENCE TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals		
Trichloromethylsilane	Sigma Aldrich	Cat# 488712
Hexadecane	Sigma Aldrich	Cat#H6703
Ethanol	Sigma Aldrich	Cat# 493511
1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane	Alfa Aesar	Cat#L16584
n-Hexane	Fischer Chemicals	Cat#296090
Cyclohexane	VWR	Cat#BDH1111-4LG
Toluene	Sigma Aldrich	Cat#676756
Karl-Fischer reagent	Merk	Cat#1.09255
Milli-Q water	Sartorius	https://www.sartorius.com/shop/ww/en/eur/applications-laboratory-lab-water-purification/arium-pro-vf-ultrapure-water-system/p/H2OPRO-VF-T-TOC
Software and algorithms		
OCA-Software	Data Physics	https://www.dataphysics-ics-instruments.com/products/oca/software/#SCA20
Instruments		
Oxygen plasma chamber (Diener Electronic Femto)	Diener Electronic	https://www.plasma.com/en/
Mettler Toledo C20 compact KF	Mettler Toledo	https://www.mt.com/ch/en/home/phased_out_products/Laboratory_Analytics_Browse/Product_Family_Browse_titrators_main/Product_Family_KF_Titrators_main/C20_Compact_KF_Coulometer_1.html
Data Physics OCA35 goniometer	Data Physics	https://www.dataphysics-ics-instruments.com/products/oca/